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# (54) Polymeric blends

(57) Reinforced blends of polyamides such as nylons, especially nylon 6 : 6, and crystalline polyolefins, particularly polypropylene comprising 50 to 95% by weight polymer and 5 to 50% by weight glass fibre, in which the polymeric component comprises at least 50% by weight of at least one polyamide such as nylon, particularly nylon 6, 6, and crystalline polyolefin such as polypropylene, and preferably also up to 10% by weight of a graft copolymer derived from a crystalline polyolefin; the graft copolymer being obtained by grafting functional groups, especially maleic anhydride residues, onto the crystalline polyolefin polymer and acting to compatibilise the blend, have improved heat distortion temperatures.

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Polymeric Blends

This invention relates to polymeric blends and in particular, to polyamide/polyolefin blends.

Reinforced polyamide/polyolefin blends are known valuable raw materials (both without and with additives such as stabilisers, lubricants or mineral or other fillers) which have many applications. One of the important physical properties of reinforced polymeric blends, which often determines the suitability of the blend for use in a given application, is its heat distortion temperature (hereinafter HDT). Surprisingly, the Applicants have found that selected reinforced polyamide/polyolefin blends have HDT's which are significantly higher than the HDT's which might have been expected from a comparison of the HDT's of reinforced polyamides and reinforced polyolefins.

It is an object of the present invention to provide the aforementioned selected polyamide/polyolefin blends.

According to the present invention, a polymeric blend comprises 50% to 95% by weight of a polymeric component and 5% to 50% by weight of glass fibres, the polymeric component comprising at least one crystalline polyolefin and at least 50% by weight of at least one polyamide.

Preferably, the polymeric blend contains at least 55% by weight of polyamide, particularly between 55% and 90%, more particularly between 55% and 80%.

Preferably, the polymeric blend comprises 20% to 45% by weight of glass fibres. Alternatively, the polymeric blend comprises 8% to 30%, preferably 12% to 18%, by weight of glass fibres and mineral filler, the total amount of glass fibres and filler being in the range 25% to 45% by weight.

Preferably, the polymeric component comprises up to 10%, preferably between 1% to 5%, by weight of a graft copolymer derived from a crystalline polyolefin, the graft copolymer being obtained by grafting functional groups on to the polyolefin whereby the graft copolymer, by interaction of the functional groups with the polyamide, compatibilises the blend.

Preferably, the balance of the polymeric component comprises substantially only the crystalline polyolefin.

By "crystalline polyolefin" we mean polyolefins in which at least some of the polymer chains are assembled into crystallites. Such polyolefins give characteristic x-ray diffraction patterns and exhibit significant melting peaks in equipment such as differential scanning calorimeters.

The polyamides used in the polymeric component of blends of the invention are thermoplastic polymers obtained by polycondensation of diamines with dicarboxylic acids or by self-condensation of amino acids or lactams. More particularly, the polyamides are linear polyamides which have fibre-forming characteristics and are usually referred to as "nylon" and includes the following polymers:-

| | |
|---|---|
| polyhexamethylene adipamide | (nylon 6:6) |
| polycaprolactam | (nylon 6 ) |
| polydodecanlactam | (nylon 12 ) |
| polyhexamethylene sebacamide | (nylon 6:10) |
| polyhexamethylene isophthalamide | (nylon 6:iP) |
| polyhexamethylene terephthalamide | (nylon 6:T) |
| polymetaxylylene adipamide | (nylon MXD:6) |
| polyundecanomide | (nylon 11) |

and copolymers therefrom. Preferred polymers are polyhexamethylene adipamide and polycaprolactam and copolymers or mixtures thereof.

The crystalline polyolefin used in the polymeric component of blends of the invention includes one or more polymerised olefin monomers, for example polymers of ethylene or propylene and copolymers and block copolymers of those monomers with each other or with other olefin monomers. Preferred polymers are polypropylene and block copolymers of propylene and up to 25%, preferably up to 10%, by weight of ethylene.

The graft copolymers used in the polymeric components of blends of the invention are preferably obtained by grafting an unsaturated dicarboxylic acid or the anhydride thereof onto the polyolefin. The unsaturated acid or anhydride may be any acid or anhydride which reacts with the polyolefin to form the graft copolymer having the required compatibilising properties. Preferred compounds are maleic acid, itaconic acid or, particularly, maleic anhydride.

Preferred graft copolymers used in the polymeric components of blends of the invention are grafted using maleic anhydride. The graft copolymer preferably has both a grafted anhydride content and a residual free anhydride content of between 0.5% to 5%, more particularly 1% to 2%, preferably 1.4% to 1.6% by weight.

Preferably, the graft copolymers are obtained by grafting the functional groups onto polyolefins of the same olefins as the crystalline polyolefin. Although the polymers used in the grafting process need not be identical to the other polyolefins, they are preferably of the same general type. Preferably, the graft copolymer is derived from polypropylene or block copolymers of propylene and up to 25%, preferably up to 10%, by weight of ethylene.

Preferably, the glass fibres are E glass filaments suitably coated with a size compatible with polyamides or polyolefins, particularly polyamides, and chopped as bundles of many filaments into lengths typically in the range 1.5 mm to 100 mm, preferably 2.5 mm to 25 mm and more particularly 2.5 mm to 7 mm. Alternatively, suitably sized continuous glass rovings can be fed into the compounding extruder with the polymer or into the melt, the rovings being broken into short lengths during compounding.

The mineral filler can be any suitable filler and typically is powdered calcium carbonate, talc, mica or a clay mineral.

The invention is illustrated by reference to the following Examples and to Tables 1 to 4, which tables being described in more detail below.

<u>Example 1</u>

Comparative blends 1 to 3 were selected from commercially-available reinforced polymeric compounds.

Blends 1 and 3 were MARANYL A175 black and natural (trade name of Imperial Chemical Industries plc, "ICI") which are nylon 6:6 compounds nominally containing 30% by weight of glass fibres, and blend 2 was PROCOM GC 30S 401 (trade name of ICI) which is an elastomer modified polypropylene nominally containing 30% by weight of glass fibres.

Drying of the pellets of these compounds was carried out in accordance with the supplier's instructions. The pellets were then moulded into the required test pieces using conventional screw pre-plasticising injection moulding machines in accordance with the supplier's recommendations as to moulding conditions.

The test pieces of compounds 1 to 3 were then tested in accordance with the test procedures outlined below.

Example 2

For each of the blends 4 (also comparative) and 9 and 10 (both in accordance with the invention), the constituents of the polymeric component were tumble-mixed together with the chopped glass fibres and, when present, the mineral filler to form a substantially homogenous dry blend. The dry blend was then metered into the feed pocket of a single screw compounding extruder (Plaston) which had a vented barrel of 38 mm (1.5 inch) internal diameter and terminated in a lace extrusion die. The extruder screw had a length to diameter ratio of 30 and had a straight-through configuration which included two compression zones (of the parallel-stepped compression type completed in half a turn - compression ratio approximately 3.6:1) separated by a vented decompression zone (vacuum being applied to the vent port during compounding).

The dry blends were fed to the extruder at a rate sufficient to keep the exposed part of the screw at the base of the feed pocket just covered with the respective dry blend at the screw rotational speed used in each case. Typically, the speed was about 120 rpm giving a blend feed rate of about 12 kg/hr. Typically, the set barrel temperatures ranged from 240°C to 250°C at the hopper end to 275°C to 285°C at the die end. The reduced pressure applied to the vent port was less than ambient atmospheric pressure by at least 635 mm (25 inches) of mercury.

The extruded laces were water-bath quenched, superficially dried and cut into pellets. The pellets were vacuum oven dried under reduced pressure at about 90°C for 18 hours. The pellets were then moulded into the required test pieces using conventional screw pre-plasticising injection moulding machines. Typically, the set barrel temperatures ranged from about 260°C to 275°C at the hopper end to about 275°C to 290°C at the nozzle end. The moulds were water or oil heated to about 80°C. Other moulding machine settings were chosen to give good quality test pieces.

The test pieces of blends 4, 9 and 10 were then tested in accordance with the test procedures outlined below.

Example 3

For each of the blends 5 to 8 (all in accordance with the invention), the appropriate granular or powdered components, excluding the glass fibres, were mixed together to form a substantially homogenous dry blend. The dry blend was then metered into the primary feed pocket of a co-rotating twin-screw compounding extruder (Werner and Pfleider ZSK-30). The extruder had an approximate length to diameter ratio for each screw of 32.5:1, with a barrel length of 10 sections. The primary feed pocket was situated in barrel section 1 and the extrusion die was attached to barrel section 10. Vent ports were situated at barrel sections 4 and 9, vacuum being applied to the latter vent port. The vent port at section 4 was open to atmosphere and served as a feed port for the chopped glass fibres which were metered in steadily at the required ratio.

The co-rotating, intermeshing screws of the extruder each consisted of a similar series of Werner and Pfleider conveying or kneading components (of two start or twin lobe type) arranged to provide a conveying, melting and intimate mixing action on the blend components, decompression zones at barrel sections 4 and 9 and extrusion pressure at the extrusion die.

The materials were supplied to the respective feed pockets such that the total output rate was about 20kg/hr. Typically, the set barrel temperatures ranged from 275°C at section 1 to 285°C at section 10, actual melt temperatures being about 300°C to 305°C. The reduced pressure applied to the vent port at section 9 was less than ambient atmospheric pressure by about 710 mm (27 inches) of mercury.

The extruded laces were water-bath quenched, superficially dried and cut into pellets. The pellets were dried and moulded into the test pieces in accordance with the procedure described in Example 2.

The test pieces of blends 5 to 8 were then tested in accordance with the test procedures outlined below.

Reference is now made to the tables in which:-

Table 1 shows the relative proportions of polymeric component and filler;

Table 2 shows the relative proportions of the constituents of the polymeric component;

Table 3 identifies the specific components A and/or B used in the blends; and

Table 4 summarises the results of the test procedures (outlined below)

In Table 1, the glass fibres were chopped bundles of glass filaments approximately 4.5 mm long, individual filaments being about 10 µm in diameter and coated with size designed to be compatible with linear polyamides, particularly nylon 6:6 or nylon 6. The mineral was powdered calcium carbonate with a particle size distribution in the range 99% less than 10 µm, 44% less than 3 µm and 10% less than 1 µm.

In Table 2, the constituents are as follows:-

A is the polyamide;

B is the crystalline polyolefin; and

C is the graft copolymer and is a maleinised block copolymer of propylene and up to 10% ethylene containing about 1.5% by weight of grafted maleic anhydride and about 1.5% by weight of free anhydride. A typical preparation for such a polymer is described in GB 1403797. The same copolymer was used in all of the blends 4 to 8 in powdered form having been cryogenically ground.

In Table 4, the tests have been determined as follows:-

HDT: was determined using the method of ISO 75-1987(E) Methods A and B (using a nominal surface stress of 1.80 MPa and 0.45 MPa, respectively) using test pieces of cross-section about 12.7 mm in height and 3.2 mm thick. Prior to testing the samples were annealed at 100°C for 30 minutes by immersion in silicone oil, following which they were allowed to cool in air, except as indicated in Table 4. The HDT test was also conducted in a bath of silicone oil. was determined using the method of ISO 178 - 1975. Test pieces were

FLEXURAL MODULUS: parallel-sided centre portions of injection moulded tensile bars (as for ISO 527 - 1966(E), type 1 test specimen) about 10 mm wide x 3.2 mm thick. A span of 50 mm was used and the test machine crosshead speed was 10 mm/min.

NOTCHED IZOD: was determined using the method of ISO 180 - 1982 (E), method designation ISO 180/4A. Test pieces were 10 mm wide x 3.2 mm thick, with a standard V - notch of tip radius about 0.25 mm.

The notches were moulded into the test pieces for blend 4 and were machined into the test pieces for the other blends.

As can be seen (Table 4), blends 5 to 10 in accordance with the invention have surprisingly high HDT's when compared to the HDT's of the blends 1 to 4.

TABLE 1

| BLEND NO | POLYMERIC COMPONENT (% BY WEIGHT) | GLASS/MINERAL COMPONENT (% BY WEIGHT) | |
|---|---|---|---|
| | | GLASS | MINERAL |
| 4 | 70 | 30 | -- |
| 5 | 70 | 30 | -- |
| 6 | 70 | 30 | -- |
| 7 | 70 | 30 | -- |
| 8 | 70 | 30 | -- |
| 9 | 60 | 15 | 25 |
| 10 | 60 | 15 | 25 |

TABLE 2

| BLEND NO | POLYMERIC COMPONENT CONSTITUENTS (INCLUDING ANY STABILISERS)(% BY WT) | | |
|---|---|---|---|
| | A | B | C |
| 4 | 40 | 56 | 4 |
| 5 | 50.6* | 46.4 | 3 |
| 6 | 60 | 36 | 4 |
| 7 | 60 | 38 | 2 |
| 8 | 60.6* | 36.4 | 3 |
| 9 | 60 | 36 | 4 |
| 10 | 60 | 36 | 4 |

* includes a small quantity of polyamide stabiliser system added at the time of compounding the blend.

TABLE 3

| BLEND NO | COMPONENT (TRADE NAME OR CODE)* A | B |
|---|---|---|
| 4 | MARANYL A117 | PROPATHENE GWM 213 |
| 5 | MARANYL A117 | PROPATHENE GWM 213 |
| 6 | MARANYL A117 | PROPATHENE GWM 213 |
| 7 | MARANYL A117 | PROPATHENE GWM 213 |
| 8 | MARANYL A117 | PROPATHENE GWM 213 |
| 9 | MARANYL A117 | PROPATHENE GW 522M |
| 10 | MARANYL A117 | PROPATHENE GW 522M |

* All Trade Name or Code of ICI

NOTES: 1 MARANYL A117 is nylon 6:6 generally having a number average molecular weight of 16500 to 18000.

2 PROPATHENE GWM 213 and GW 522M are polypropylenes, the former being supplied in the form of pellets and the latter in the form of powder.

TABLE 4

| BLEND NO | HDT (°C) AT 0.45MPa | AT 1.8MPa | FLEXURAL MODULUS (GPa) | NOTCHED IZOD ($kJ/m^2$) at 23°C |
|---|---|---|---|---|
| 1 | 261 | 248 | 7.2 | 10 |
| 2 | 154 | 135 | 4.0 | 18 |
| 3 | -- | 252 | 8.1 | 9.4 |
| 4 | 171* | 158* | 5.9 | 12 |
| 5 | -- | 189 | 6.6 | 9.0 |
| 6 | 257 | 236 | 6.5 | 9.6 |
| 7 | 258 | 240 | 6.6 | 10.5 |
| 8 | -- | 240 | 6.7 | 9.2 |
| 9 | 250 | 204 | 5.6 | 6.8 |
| 10 | 249 | 200 | 5.3 | 8.1 |

When no result is quoted, the parameter was not determined.

* Bars not annealed before measuring HDT values.

CLAIMS

1 A reinforced polymeric blend comprising 50% to 95% by weight of a polymeric component and 5% to 50% by weight of glass fibres, the polymeric component comprising at least one crystalline polyolefin and at least 50% by weight of at least one polyamide.

2 A blend according to claim 1, which comprises 20% to 45% by weight of glass fibres.

3 A blend according to claim 1, which comprises 8% to 30% by weight of glass fibres and mineral filler, the total amount of glass fibres and mineral filler being in the range 25% to 45% by weight.

4 A blend according to claim 3, which comprises 12% to 18% by weight of glass fibres.

5 A blend according to claim 1, in which the polymeric component comprises at least 55% by weight of said polyamide.

6 A blend according to any one of the preceding claims, in which the polymeric component comprises 55% to 90% by weight of the polyamide.

7 A blend according to any one of the preceding claims, in which the polymeric component comprises up to 10% by weight of a graft copolymer derived from a crystalline polyolefin, the graft copolymer being obtained by grafting functional groups as to the polyolefin whereby the graft copolymer, by interaction of the functional groups with the polyamide, compatibilises the blend.

8 A blend according to claim 7, in which the polymeric component comprises 1% to 5% by weight of the graft copolymer.

9 A blend according to any one of the preceding claims, in which the balance of the polymeric component comprises substantially only the crystalline polyolefin.

10 A blend according to anyone of the preceding claims, in which the polyamide is polyhexamethylene adipamide, polycaprolactam, polydodecamlactam, polyhexamethylene sebacamide, polyhexamethylene isopthalamide, polyhexamethylene terephthalamide, polymetaxylylene adipamide or polyundecanomide or copolymers therefrom or mixtures thereof.

11 A blend according to any one of the preceding claims, in which said crystalline polyolefin is polypropylene or a copolymer of propylene with up to 25% by weight of ethylene.

12 A blend according to claim 7 and to any one of the preceding claims dependent on claim 7, in which said functional groups are derived from maleic acid, itaconic acid or maleic anhydride.

13 A blend according to claim 12, in which said functional groups are derived from maleic anhydride and in which the grafted copolymer has both a grafted anhydride content and a residual free anhydride content of between 0.5 and 5% by weight.

14 A blend according to claim 7 and to any one of the preceding claims dependent on claim 7, in which the polymer from which the graft copolymer is derived is polypropylene or a block copolymer of propylene with up to 25% by weight of ethylene.

15 A blend according to claim 1, substantially as hereinbefore described with reference to the Examples.

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